

(19) Japan Patent and Trademark Office (JP)
(12) Patent Gazette (B1) (11) Patent No. 3450323
(P3450323)
(45) Issued: September 22, 2003 (24) Registered: July 11, 2003
(51) Int Cl. ID No. F I
B 09 C 1/06 A 62 D 3/00 ZAB
A 62 D 3/00 B 09 B 3/00 303P
B 09 B 3/00 304Z

No. of Claims 13 (10 pages in original)

(21) Application No. 2002-308341 (P2002-308341)

(22) Submitted October 23, 2002

Examination Requested October 23, 2002

(31) Priority Claim No. 2002-71818 (P2002-71818)

(32) Priority Date March 15, 2002

(33) Country of Priority Japan (JP)

Application Subject to Accelerated Examination

(73) Patentee 500121126
ISV Japan Co., Ltd.
16 Ichiban-cho, Chiyoda-ku, Tokyo, Japan

(72) Inventor Toshiaki YASUFUKU
3-6-1 Kita Kubo-ji-cho, Chuo-ku, Osaka-shi,
Osaka-fu, Japan

(72) Inventor Takahiko TERADA
c/o Ube Industries, Ltd.
Energy & Environment Segment
Environmental Development Laboratory
1978-2 Oh-aza Ogushi, Ube-shi, Yamaguchi-ken,
Japan

(72) Inventor Kazuya KIGAWADA
c/o Hazama Corp.
515-1 Karima Aza Nishimuko, Tsukuba-shi,
Ibaraki-ken, Japan

(74) Agent 100074675
Yasuo YANAGIGAWA, Patent Attorney

Examiner Miki KATO

Continued on last page

(54) [Title] Pyrolytic treatment method for halogen-containing organic
compounds

(57) [Claims]

[Claim 1] A pyrolytic treatment method for halogen-containing organic compounds characterized in that soil contaminated with a halogen-containing organic compound is heated to a temperature of 300 to 600°C in the presence of activated alumina and water to dissociate the halogen constituent from said halogen-containing organic compound, said halogen constituent is captured in the mixture of soil and activated alumina, and then said mixture is melted to fix the halogen constituent inside the melt, and to chemically reduce and pyrolyze the organic compound from which the halogen constituent has been dissociated.

[Claim 2] A pyrolytic treatment method for halogen-containing organic compounds characterized in that a solid contaminated with a halogen-containing organic compound is heated together with soil to a temperature of 300 to 600°C in the presence of activated alumina and water to dissociate the halogen constituent from said halogen-containing organic compound, said halogen constituent is captured in the mixture of soil and activated alumina, and then said mixture is melted to fix the halogen constituent inside the melt, and to chemically reduce and pyrolyze the organic compound from which the halogen constituent has been dissociated.

[Claim 3] A pyrolytic treatment method for halogen-containing organic compounds characterized in that a liquid, powder, or mass of halogen-containing organic compound or containing a halogen-containing organic compound is heated together with soil to a temperature of 300 to 600°C in the presence of activated alumina and water to dissociate the halogen constituent from said halogen-containing organic compound, said halogen constituent is captured in the mixture of soil and activated alumina, and then said mixture is melted to fix the halogen constituent inside the melt, and to chemically reduce and pyrolyze the organic compound from which the halogen constituent has been dissociated.

[Claim 4] The pyrolytic treatment method for halogen-containing organic compounds disclosed in any of claims 1 through 3 characterized in that the activated alumina has pores on its surface.

[Claim 5] The pyrolytic treatment method for halogen-containing organic compounds disclosed in any of claims 1 through 4 characterized in that the specific surface area of the activated alumina is in the range of 50 to 500m²/g.

[Claim 6] The pyrolytic treatment method for halogen-containing organic compounds disclosed in any of claims 1 through 5 characterized in that the reduction pyrolysis product from the organic compound is exhausted to the outside after being oxidized.

[Claim 7] The pyrolytic treatment method for halogen-containing organic compounds disclosed in any of claims 1 through 6 characterized in that melting of the mixture is accomplished using Joule heat generated by flowing electrical current between two or more electrodes embedded in said mixture.

[Claim 8] The pyrolytic treatment method for halogen-containing organic compounds disclosed in any of claims 1 through 7 characterized in that melting of the mixture is executed inside a hole formed in the ground.

[Claim 9] The pyrolytic treatment method for halogen-containing organic compounds disclosed in any of claims 1 through 7 characterized in that melting of the mixture is executed inside a container moveably installed on the ground.

[Claim 10] The pyrolytic treatment method for halogen-containing organic compounds disclosed in any of claims 1 through 9 characterized in that the halogen-containing organic compound is a chlorine-containing organic compound.

[Claim 11] A pyrolytic treatment method for halogen-containing organic compounds characterized in that soil contaminated with a halogen-containing organic compound is heated to a temperature of 300 to 600°C in the presence of a metal oxide powder with pores in its surface and water to dissociate the halogen constituent from said halogen-containing organic compound, said halogen constituent is captured in the mixture of soil and metal oxide powder, and then said mixture is melted to fix the halogen constituent inside the melt, and to chemically reduce and pyrolyze the organic compound from which the halogen constituent has been dissociated.

[Claim 12] A pyrolytic treatment method for halogen-containing organic compounds characterized in that a solid contaminated with a halogen-containing organic compound is heated together with soil to a temperature of 300 to 600°C in the presence of a metal oxide powder with pores in its surface and water to dissociate the halogen constituent from said halogen-containing organic compound, said halogen constituent is captured in the mixture of soil and metal oxide powder, and then said mixture is melted to fix the halogen constituent inside the melt, and to chemically reduce and pyrolyze the organic compound from which the halogen constituent has been dissociated.

[Claim 13] A pyrolytic treatment method for halogen-containing organic compounds characterized in that a liquid, powder, or mass of halogen-containing organic compound or containing a halogen-containing organic compound is heated together with soil to a temperature of 300 to 600°C in the presence of a metal oxide powder with pores in its surface and water to dissociate the halogen constituent from said halogen-containing organic compound, said halogen constituent is captured in the mixture of soil and metal oxide powder, and then said mixture is melted to fix the halogen constituent inside the melt, and to chemically reduce and pyrolyze the organic compound from which the halogen constituent has been dissociated.

[Detailed Description]

[0001]

[Pertinent Technical Field] This invention pertains to a pyrolytic treatment method for halogen-containing organic compounds.

[0002]

[Prior Art] Halogen-containing organic compounds have been widely used in the past as agricultural chemicals (pesticides), insulation, detergents, and fire retardants, but since their use has been rejected in recent years due to environmental problems, the production and use of halogen-containing organic compounds has currently nearly completely stopped. However, halogen-containing organic compounds are generally chemically and thermally stable substances, and the fact that halogen-containing organic compounds that have been used in the past remain in the soil for long periods of time poses environmental

problems. Because of this, there is a desire to promptly break down and detoxify the halogen-containing organic compounds in contaminated soil. Soil, or solids, such as combustion ash or fly ash, etc., that has been contaminated with dioxins unintentionally produced by the incineration of garbage has also become a problem in areas surrounding municipal garbage incinerators. Therefore, a great deal of research is being conducted aimed at detoxifying soil, etc. that has been contaminated by organic compounds.

[0003] A method is disclosed in patent citation 1 as a method of detoxifying sediment or soil that has been contaminated with organic contaminants and inorganic substances, wherein the sediment or soil is mixed with raw aluminum oxide, alumina, iron oxide, and flux and heated, melted, and then cooled to produce an amorphous substance (vitrified mass).

[0004] A method is disclosed in patent citation 2 as a method of detoxifying combustion ash or fusion ash contaminated with hazardous organic compounds, such as dioxins, etc., wherein the combustion ash or fusion ash is mixed with SiO_2 or Al_2O_3 and heated.

[0005]

[Patent Citation 1] Japan Patent Publication No. 2001-506964

[Patent Citation 2] Japan Kokai Patent Publication No. 2000-51818

[0006]

[Problems to be Solved] Soil or solids that have been contaminated with halogen-containing organic compounds can be detoxified by heating the soil or solid and pyrolyzing the halogen-containing organic compounds. In addition, halogen-containing organic compounds or liquids, powders, or masses containing them, such as agricultural chemicals, etc. can be similarly heated and pyrolyzed. However, even when halogen-containing organic compounds are heated and pyrolyzed once, if halogen constituents (especially chlorine) and/or organic compounds (especially benzene) are present in the decomposition off-gas, dioxins may be produced.

[0007] Consequently, the purpose of this invention is to provide a method that can pyrolyze the halogen-containing organic compounds in soil that has been contaminated by halogen-containing organic compounds without discharging

halogen constituent gas (especially chlorine gas) and/or organic compounds (especially benzene) to the outside as much as possible. The purpose of this invention also is to provide a method that can pyrolyze the halogen-containing organic compounds in solids that have been contaminated by halogen-containing organic compounds without discharging halogen constituent gas and/or organic compounds to the outside as much as possible. The purpose of this invention is further to provide a method that can pyrolyze the halogen-containing organic compounds in halogen-containing organic compounds or liquids, powders, or masses that contain halogen-containing organic compounds without discharging halogen constituent gas and/or organic compounds to the outside as much as possible.

[0008]

[Means of Solution] The inventors discovered that, by heating soil contaminated with a halogen-containing organic compound to a temperature of 300 to 600°C together with, and in the presence of, activated alumina or a metal oxide powder with pores in its surface and water to dissociate the halogen constituent (especially chlorine) from said halogen-containing organic compound, capturing said halogen constituent in the mixture of soil and activated alumina or metal oxide powder with pores in its surface, and then melting said mixture to fix the halogen constituent inside said melt, the amount of the halogen constituent in the decomposition off-gas could be reduced, and that, by chemically reducing and pyrolyzing the organic compound from which the halogen constituent had been dissociated (especially benzene) in the presence of water, the organic compound could be efficiently decomposed and the amount of the organic compound in the decomposition off-gas could be decreased, and arrived at this invention.

[0009] This invention is a pyrolytic treatment method for halogen-containing organic compounds characterized in that soil contaminated with a halogen-containing organic compound is heated to a temperature of 300 to 600°C in the presence of activated alumina or a metal oxide powder with pores in its surface and water to dissociate the halogen constituent from said halogen-containing organic compound, said halogen constituent is captured in the

mixture of soil and activated alumina or metal oxide powder with pores in its surface, and then said mixture is melted to fix the halogen constituent inside the melt, and to chemically reduce and pyrolyze the organic compound from which the halogen constituent has been dissociated.

[0010] This invention is also a pyrolytic treatment method for halogen-containing organic compounds characterized in that a solid contaminated with a halogen-containing organic compound is heated together with soil to a temperature of 300 to 600°C in the presence of activated alumina or a metal oxide powder with pores in its surface and water to dissociate the halogen constituent from said halogen-containing organic compound, said halogen constituent is captured in the mixture of soil and activated alumina or metal oxide powder with pores in its surface, and then said mixture is melted to fix the halogen constituent inside the melt, and to chemically reduce and pyrolyze the organic compound from which the halogen constituent has been dissociated. The soil used in heating with the contaminated solid here refers to inorganic matter produced by the decomposition of rock, etc. on the surface of the earth, and may or may not contain organic matter, such as decayed matter, etc.

[0011] This invention is further a pyrolytic treatment method for halogen-containing organic compounds characterized in that a liquid, powder, or mass of halogen-containing organic compound or containing a halogen-containing organic compound is heated together with soil to a temperature of 300 to 600°C in the presence of activated alumina or a metal oxide powder with pores in its surface and water to dissociate the halogen constituent from said halogen-containing organic compound, said halogen constituent is captured in the mixture of soil and activated alumina or metal oxide powder with pores in its surface, and then said mixture is melted to fix the halogen constituent inside the melt, and to chemically reduce and pyrolyze the organic compound from which the halogen constituent has been dissociated. The soil used in heating with the contaminated solid here refers to inorganic matter produced by the decomposition of rock, etc. on the surface of the earth, and may or may not contain organic matter, such as decayed matter, etc.

[0012] Preferred embodiments of the pyrolysis treatment method for halogen-containing organic compounds of this invention are as follows.

- (1) The activated alumina possesses pores in its surface.
- (2) The metal oxide powder is activated alumina.
- (3) Melting of the mixture is accomplished using Joule heat generated by flowing electrical current between two or more electrodes embedded in said mixture.
- (4) Melting of the mixture is executed inside a hole formed in the ground.
- (5) Melting of the mixture is executed inside a container moveably installed on the ground.
- (6) The halogen-containing organic compound is a chlorine-containing organic compound.

[0013]

[Embodiment] The halogen-containing organic compounds that are the object of decomposition processing in the method of this invention are not specifically limited. The method of this invention is especially utile in the decomposition processing of halogen-containing organic compounds whose volatilization temperature (boiling point) is 100°C or higher (especially 100 to 300°C), typical examples of which could include organic chlorine agricultural chemicals, such as hexachlorobenzene (HCB), hexachlorocyclohexane (BHC), p,p'-dichlorodiphenyltrichloroethane (DDT), chlordane, and endrin, etc., biphenyl polychloride (PCB), and dioxins.

[0014] In this invention, the halogen-containing organic compound is heated together with soil in the presence of activated alumina or a metal oxide powder with pores in its surface and water.

[0015] It is preferred that the activated alumina pores in its surface to facilitate efficient capture of the halogen constituent dissociated from the halogen-containing organic compounds. Activated alumina (alumina whose main constituent is γ -alumina) can be given as a typical example of a metal oxide powder with pores in its surface. Activated alumina acts as a decomposition promoter. It is preferred that the activated alumina used in the method of

this invention have a specific surface area in the range of 50 to 500 m²/g, especially 50 to 300 m²/g.

[0016] A method of adding water or a compound, that will produce water vapor when heated to the soil in advance can be given as an example of a method for causing water to be present when the halogen-containing organic compounds is heated together with soil. Water retentive substances, such as bentonite, etc., or metal hydroxides can be listed as examples of compounds that generate water vapor when heated. Sodium hydroxide, magnesium hydroxide, potassium hydroxide, and aluminum hydroxide can be listed as examples of metal hydroxides. In addition, a method wherein an input port for supplying water vapor or water to the melt furnace that will be hot melting the soil, and supplying water vapor or water during the execution of hot melting the soil can be given as another method for causing water to be present in the soil when it is heated.

[0017] An alkali metal compound or alkali earth metal compound, which acts as a melting point (glass transition temperature) depressant for the soil, may be further added to the soil. Sodium carbonate, magnesium carbonate, and potassium carbonate, and sodium hydroxide, magnesium hydroxide, and potassium hydroxide can be listed as examples of alkali metal compounds and alkali earth metal compounds.

[0018] The pyrolytic treatment method for halogen-containing organic compounds in contaminated soil will be explained below, using contaminated soil as the object of treatment as an example. Soil from agricultural land on which organic chlorine agricultural chemicals, such as HCB, BHC, DDT, chlordane, and endrin, etc., have been spread, soil surrounding factories that manufactured or used halogen-containing organic compounds, and dioxin-contaminated soil surrounding municipal garbage incinerators can be listed as examples of contaminated soil that are the object of treatment in the method of this invention. The amount of halogen-containing organic compounds in the contaminated soil is normally in the range of 0.01 to 50% by mass, especially 1 to 50% by mass, and more especially 2 to 40% by mass.

[0019] First, activated alumina or a metal oxide powder with pores in its surface, and further, as necessary, water or a compound that generates water vapor when heated, and an alkali metal compound or, alkali earth metal compound as a melting point depressant, are admixed into the contaminated soil to obtain a contaminated soil mixture. Instead of the activated alumina or metal oxide powder with pores in its surface, a compound that will produce activated alumina or a metal oxide powder with pores in its surface at temperatures of 600° or lower may be added. Aluminum hydroxide that produces activated alumina or a metal oxide powder with pores in its surface at temperatures of 600° or lower can be given as a typical example of this compound.

[0020] A commonly known mixer, such as a drum mixer or paddle mixer, etc. can be used to mix the contaminated soil and the activated alumina or metal oxide powder with pores in its surface. The amount of activated alumina or a metal oxide powder with pores in its surface added differs depending on the content of halogen-containing organic compound in the contaminated soil, but it is generally in the range of 0.1 to 100 parts by mass, preferably in the range of 1 to 50 parts by mass, per 100 parts by mass contaminated soil. In addition, using the amount of halogen-containing organic compound in the contaminated soil as a reference, the amount of activated alumina or metal oxide powder with pores in its surface added is in the range of 0.1 to 1,000 parts by mass, preferably in the range of 1 to 500 parts by mass, per 100 parts by mass halogen-containing organic compound.

[0021] Next, the contaminated soil mixture is heated, causing the halogen constituent to dissociate from the halogen-containing organic compound, the halogen constituent is captured in the mixture of soil and activated alumina or metal oxide powder with pores in its surface, and then that mixture is melted, fixing the halogen constituent in the melt, after which the organic compound from which the halogen constituent was dissociated is chemically reduced and pyrolyzed. It is preferred that this series of heating operations be executed using a single melt furnace.

[0022] It is preferred that melting of the contaminated soil mixture be performed by a method wherein a whole formed in the ground or a heat resistant

container moveably disposed on the ground is filled with the contaminated soil mixture, and the contaminated soil mixture filling is heated and sequentially melted from the top to the bottom. It is preferred, that a method in which Joule heat generated by flowing electrical current between two or more electrodes embedded in the contaminated soil mixture be used as the method of heating and melting the mixture. Even when heating of the aforementioned contaminated soil is executed inside a hole formed in the ground, it is preferred, taking into consideration the contamination of the surrounding soil, that a container be installed in the ground in advance, and that heating be executed inside that container.

[0023] The method employing Joule heat to the contaminated soil mixture will be explained below, referring to the attached figures.

[0024] First, a heat resistant container is filled with the contaminated soil mixture, as shown in Figure 1. The density with which the container 2 is filled with the contaminated soil mixture 1 is generally in the range of 1 to 2 tons/m³. It is preferred that the volume of contaminated soil mixture 1 filling the container 2 generally be 1 m³ or more (especially 5 to 10 m³). The shape of the opening in the heat resistant container 2 can be a variety of shapes, such as square, a square with truncated corners (octagonal), or circular, etc., but a square with truncated corners is preferred.

[0025] In Figure 1, the heat resistant container 2 has a two-layer construction with an inner container 3 and an outer container 4. It is preferred that the inner container 3 be formed of a ceramic powder, such as silica sand (silicon dioxide powder), etc. The thickness of the container gets progressively thicker in the downward direction in order to increase heat resistance. This is because the heat of the molten soil tends to spread laterally as the melt advances downward. It is preferred that the thickness of the inner container 3 generally be in the range of 10 to 20 cm at the top (the thinner portion), and the thickness at the bottom (the thicker portion) be 1.1 to 2 times as thick as the top portion.

[0026] It is preferred that the outer container 4 be formed of a material with low gas permeability so that the decomposition products of the halogen-

containing organic compounds do not disperse to the outside. Fireproof brick, fireproof castables, and various thermal insulators (e.g., ceramic fiber, calcium silicate, perlite, rock wool, asbestos, diatomaceous earth, glass wool, magnesium carbonate), etc. can be given as examples of this material.

[0027] Next, a covering soil layer 5 is formed on top of the contaminated soil mixture 1, covering the halogen-containing organic compound, as shown in Figure 2 and Figure 3, with soil that substantively contains no halogen-containing organic compounds. An initial conductivity resistance path 6 to convert electrical energy into thermal energy (Joule heat), and the electrodes 7 to supply electrical energy to the initial conductivity resistance path 6, are disposed on the covering soil layer 5 in that order. Figure 2 is a sectional diagram of an example of a container in which a covering soil layer, initial conductivity resistance strip, and electrodes have been disposed on top of a contaminated soil mixture, and Figure 3 is a plan-view diagram seen from the top of the heat resistant container in Figure 2.

[0028] The covering soil layer 5 has the function of melting before the contaminated soil mixture and uniformly heating the entire surface of the contaminated soil mixture 1. By providing a covering soil layer 5, the contaminated soil mixture 1 can be uniformly heated and melted. The thickness of the covering soil layer 5 is generally in the range of 1 to 100 cm, preferably in the range of 10 to 60 cm. The composition of the soil used in the covering soil layer 5 is not specifically limited, as long as it is soil that substantively contains no halogen-containing organic compounds.

"Substantively contains no halogen-containing organic compounds" here means that the content of halogen-containing organic compounds is less than 0.01% by mass. An aluminum compound that produces aluminum oxide when heated, or a silicon compound that produces silicon oxide when heated, or metallic aluminum, may also be added to the soil used in the covering soil layer 5.

[0029] The initial conductivity resistance strip 6 is a square plate that is disposed so that it is in contact with the four electrodes 7a, 7b, 7c, 7d, as shown in Figure 3. The initial conductivity resistance strip 6 does not necessarily have to be a plate, and could as well be a rod-shaped body. If

rod-shaped initial conductivity resistance strips 6 were used, the initial conductivity resistance strips would be disposed so that they were in electrical contact with the electrodes 7a, 7b, 7c, 7d.

[0030] The material of the initial conductivity resistance strip 6 is not specifically limited, as long as it functions to convert electrical energy into thermal energy (Joule heat). Graphite and mixtures of graphite and soil a melting point depressant can be given as examples of materials for the initial conductivity resistance strip 6. Alkali salts, such as sodium hydroxide and sodium carbonate, and glass flit can be given as examples of soil melting point depressants.

[0031] The electrodes 7a, 7b, 7c, 7d are attached to an electrode feed device (not shown) that makes it possible to move their tips vertically. Metals, such as graphite and molybdenum, etc. can be listed as examples of the material for the electrodes 7. Electrodes 7a and 7{d}, and electrodes 7b and 7c, which are disposed on diagonal lines, for respective pairs, whereby uniform electrical energy can be supplied to the initial conductivity resistance strip by supplying alternating current voltages with a 90° phase difference between them to the respective pairs.

[0032] Next, the opening of the container 2 is covered with a hood, as shown in Figure 4. Figure 4 is a sectional diagram of an example of a container covered by a hood. In Figure 4, the hood 8 is equipped with an air inlet port 9 in its side and an exhaust port 10 in its top. Hot air with a temperature of 300°C or higher (normally 300 to 800°C) is supplied to the air inlet port 9 so that the decomposition products of the halogen-containing organic compound do not produce dioxins inside the hood 8. The exhaust port 10 is an exhaust port for the decomposition product gases from the halogen-containing organic compound. It is preferred that the hood 8 be formed from a material with low gas permeability so that the decomposition product gases from the halogen-containing organic compound are not dispersed to the outside. Metals, such as steel or stainless steel, etc., can be listed as examples of that material.

[0033] Next, the electrodes 7 are connected to an electrical energy supply device, an air heating device is connected to the air inlet port 9 of the hood, and a gas treatment device is connected to the exhaust port 10.

[0034] Figure 5 is a schematic diagram showing an example of the configuration of a contaminated soil mixture treatment system that uses a melt furnace (electric resistance furnace) constructed by the process shown in Figures 1 through 4. In Figure 5, the contaminated soil mixture treatment system comprises a melt furnace 11, an electrical energy supply device to supply electrical energy to the melt furnace 11, a gas treatment device to process the gases exhausted from the melt furnace 11, and an air supply device to regulate the high-temperature air sent to the melt furnace 11. The electrical energy supply device 12 comprises private power generator equipment consisting of a generator 15 and a transformer 16. The gas treatment device 13 comprises secondary heating equipment 17, a cooler-dust arrester-cleaner (Venturi scrubber) 18, a HEPA filter, and an activated charcoal filter 20.

[0035] The electrical energy supply device 12 uses the transformer 16 to regulate the electrical energy produced by the generator 15 to a specified power level, and supplies this to the melt furnace 11. The electrical energy supplied to the melt furnace 11 is sent through the electrodes 7 to the initial conductivity resistance path [6]. The initial conductivity resistance strip 6 converts the electrical energy to thermal energy (Joule heat). The soil in the covering soil layer 5 is heated and melted by this heat.

[0036] Figure 6 shows the heat distribution in the soil mixture when the covering soil layer is melted. In Figure 6, the contaminated soil mixture 1 is heated by the covering soil layer melt 5a, and is divided into a zone 1a that has been heated to over 300°C, a zone 1b that has been heated to 100°C to 300°C, and a zone 1c below 100°C. The temperature of the covering soil layer melt 5a is over 1,300°C (normally, 1,300 to 1,600°C). The halogen-containing organic compound and water in the contaminated soil mixture in zone 1b is volatilized, detoxifying the contaminated soil. The volatilized halogen-containing organic compound is heated to a temperature over 300°C (normally 300°C to 600°C) in zone 1a, dissociating the halogen constituent in the

halogen-containing organic compound. The halogen constituent dissociated from the halogen-containing organic compound is captured in the mixture of soil and activated alumina or a metal oxide powder with pores in its surface (primarily in the activated alumina or a metal oxide powder with pores in its surface). The mixture with the captive halogen constituent is then further heated to over 1,300°C and becomes a melt, but all or a majority of the halogen constituent captured in the mixture is fixed in the melt. Meanwhile, the organic compound from which the halogen constituent has been dissociated is chemically reduced and pyrolyzed in the presence of water to produce carbon monoxide and hydrogen. This carbon monoxide gas and hydrogen gas are oxidized by the oxygen in the high-temperature air introduced from the air inlet port 9, respectively become carbon dioxide and water (water vapor).

[0037] After the entire amount of contaminated soil mixture has been melted, the supply of electrical energy to the melt furnace 11 is stopped, and the molten soil cools to form a vitrified mass. The halogen constituent that had been fixed in the melt is sealed in state in the resulting vitrified mass. However, since the vitrified mass substantively contains no halogen-containing organic compounds, and is physically and chemically stable, it can be pulverized and used as recycled crushed rock, or the like.

[0038] The treatment of the decomposition off-gas produced by the aforementioned heat treatment will be explained, referring to Figure 5. The decomposition off-gas is sent from the exhaust port 10 of the hood 8 to the gas treatment device 13.

[0039] The secondary heating equipment 17 heats the decomposition off-gas to a temperature over 850°C (normally, 900 to 1,000°C) for two seconds or more. This heating oxidizes and pyrolyzes the volatilized gases of the halogen-containing organic compound and the organic compounds (e.g., benzene, dioxins) that exist in trace amounts in the decomposition off-gas. The cooler-dust arrester-cleaner 18 rapidly cools the decomposition off-gas heated by the secondary heating equipment 17 to under 100°C, neutralizing the acidic gas, such as hydrogen halide gas, etc. contained therein and removing particulate matter. The HEPA filter 19 and activated charcoal filter 20 further recover

the extremely trace amounts of volatilized gases of the halogen-containing organic compound and the organic compounds that still exist in the decomposition off-gas. The decomposition off-gas treated by the gas treatment device 13 is then released to the outside.

[0040] The method of this invention was described above, using the typical example of contaminated soil mixture and as the object of treatment, but solids contaminated by halogen-containing organic compounds, and liquids, powders, or masses of halogen-containing organic compound or that contain halogen-containing organic compounds, can be similarly treated.

[0041] Namely, in the case that the object of treatment is a contaminated solid, treatment can be executed, e.g., as follows. First, a contaminated solid mixture is obtained by admixing [the contaminated solid together with] activated alumina or a metal oxide powder with pores in its surface, or a substance that will produce activated alumina or a metal oxide powder with pores in its surface when heated, and as necessary, water or a compound that will produce water vapor when heated, and an alkali metal compound or alkali earth metal compound as a melting point depressant to soil that substantively contains no halogen-containing organic compounds, or in which the halogen-containing organic compound content is low. "In which the halogen-containing organic compound content is low" here means that the halogen-containing organic compound content is in the range of 0.01 to 1% by mass. This contaminated solid mixture is then heated in the same manner as the aforementioned contaminated soil mixture, fixing the halogen constituent of the halogen-containing organic compound in the melt of the mixture, and chemically reducing and pyrolyzing the organic compound constituent. The amount of soil used per 1 part by mass of halogen-containing organic compound is generally in the range of 1 to 10,000 parts by mass, preferably in the range of 1 to 100 parts by mass.

[0042] PCB-containing containers, combustion ash and fly ash exhausted from municipal garbage incinerators, fireproof material (bricks) from municipal garbage incinerators, and sludge discharged from factories that

manufactured or used organic compounds can be given as examples of contaminated solids that are the object of treatment in this invention.

[0043] In cases that the object of treatment is liquids, powders, or masses of halogen-containing organic compounds or that contain halogen-containing organic compounds, treatment can be executed, e.g., as follows. First, a mixture is obtained by admixing the liquid, powder, or mass of halogen-containing organic compound or that contains a halogen-containing organic compound, activated alumina or a metal oxide powder with pores in its surface, or a substance that will produce activated alumina or a metal oxide powder with pores in its surface when heated, and as necessary, water or a compound that will produce water vapor when heated, and an alkali metal compound or alkali earth metal compound as a melting point depressant to soil that substantively contains no halogen-containing organic compounds, or in which the halogen-containing organic compound content is low. This mixture is then heated in the same manner as the aforementioned contaminated soil mixture, fixing the halogen constituent of the halogen-containing organic compound in the melt of the mixture, and chemically reducing and pyrolyzing the organic compound constituent. The amount of soil used per 1 part by mass of halogen-containing organic compound is generally in the range of 1 to 10,000 parts by mass, preferably in the range of 1 to 100 parts by mass.

[0044] In cases in which the liquid, powder, or mass of halogen-containing organic compound or that contains a halogen-containing organic compound is inside a container, with this invention, the container itself can be mixed with soil and treated. For example, transformers or capacitors in which PCB is used can be mixed as is with soil and treated. Agricultural chemicals (pesticides), insulation, detergents, and fire retardants that contain halogen-containing organic compounds as their active ingredients can be listed as examples of liquids, powders, or masses that contain halogen-containing organic compounds that are the object of treatment in this invention.

[0045] Situations are described in Figures 1 through 5 in which Joule heat is employed to hot melt the contaminated soil mixture, but the method of

hot melting the contaminated soil mixture is not specifically limited, as long as the contaminated soil mixture charged into a melt furnace can be sequentially heated and melted from the top to the bottom. For example, plasma may also be used to hot melt the contaminated soil mixture.

[0046]

[Example Embodiment] An example embodiment of this invention will be described below. Further, the constituents of the soil used in this example embodiment are as follows.

[0047]

[Table 1]

Table 1

Al ₂ O ₃	11.1% by mass
CaO	4.2% by mass
K ₂ O	2.6% by mass
MgO	2.1% by mass
MnO	0.04% by mass
Na ₂ O ₂	3.7% by mass
P ₂ O ₅	0.04% by mass
SiO ₅	61.4% by mass
TiO ₂	0.7% by mass
Fe ₂ O ₃	4.5% by mass
Halogen-containing organic compound	< 0.01% by mass

[0048] [Example Embodiment 1] 385 kg soil, 107 kg activated alumina (specific surface area: 50 m²/g), 52 kg sodium carbonate, 91 kg calcium carbonate, 285 kg pulverulent hexachlorobenzene (HCB), and 55 kg water were charged in that order into drum barrels (capacity: 2m³). Next, the drum barrels were sealed with lids and each drum barrel was mounted in a rotary mixer and rotated to prepare the mixture.

[0049] The entire amount of the resulting mixture (975 kg) was loaded into the heat resistant container 2 with an opening in its top shown in Figure 1 (opening size: 1.1 m long × 1.1 m wide × 1.5 m deep). Next, the top of the mixture is covered with soil of the composition shown in Table 1 to form a 40 cm-thick covering soil layer 5, after which an initial conductivity resistance strip 6 (material: mixture of graphite and glass flit) was embedded in the covering soil layer 5 and four electrode 7a, 7b, 7c, 7d (diameter: 100 mm)

were disposed in the initial conductivity resistance strip 6. A hood 8 equipped with an air inlet port 9 and an exhaust port 10 was then installed above the heat resistant container 2, as shown in Figure 4.

[0050] The temperature inside the hood 8 was regulated at 500°C by sending 500°C hot air into the air inlet port of the hood. Respective alternating current voltages were then impressed between electrodes 7a and 7d and electrodes 7b and 7c, supplying electrical energy to the initial conductivity resistance strip and heating the covering soil layer to create a 1,300°C melt and heating the mixture to a temperature of 300°C to 600°C. Further electrical energy continued to be supplied to the melt, heating the mixture and causing it to melt. After the entire amount of the mixture was melted, the supply of electrical energy was stopped and the molten mixture was cooled and solidified into a vitrified mass.

[0051] During the time from starting the supply of electrical energy to the initial conductivity resistance strip to solidification into a vitrified mass, the HCB decomposition rate (%) was confirmed at 99.5% by mass, as calculated by the following equation from the HCB quantity (P) in the exhaust gas discharged from the hood exhaust port and the HCB quantity (A₁) in the vitrified mass after treatment. The results of analyzing the constituents of the exhaust gas also revealed that it was mostly carbon dioxide and water.

[0052]

[Equation 1] HCB decomposition rate (%) = $\{1 - (P+A_1)/A_0\} \times 100$
Wherein, P is the HCB quantity (kg) in the exhaust gas, A₁ is the HCB quantity (kg, except that this amount was essentially 0 [zero] in the vitrified mass, and A₀ is the HCB quantity (285 kg) in the untreated mixture.

[0053] [Example Embodiment 2] A mixture was prepared using a chlordane emulsion as the halogen-containing organic compound by the same operation as in the aforementioned example embodiment 1, except that the mixture portions were 540 kg soil, 362 kg activated alumina (specific surface area: 300 m²/g), 140 kg chlordane emulsion (approximately 35 kg chlorine content), and 277 kg water.

[0054] The entire amount of the resulting mixture (6,183 kg) was heated and melted by the same operation as in example embodiment 1, except that a heat resistant container with an opening size of 1.7 m long × 1.7 m wide × 1.6 m deep was used.

[0055] A chlordane decomposition rate of 99.9999% by mass was confirmed as the result of measurements by the same method as in example embodiment 1. IN addition, the constituents of the exhaust gas were confirmed to be mostly carbon dioxide and water. Furthermore, the results of fluorescent X-ray measurement of the chlorine content in the vitrified solid confirmed that 25 kg of chlorine were fixed in the vitrified mass, and approximately 71% by mass of the chlorine in the chlordane was fixed in the vitrified mass.

[0056]

[Effect] Since the halogen constituent in a halogen-containing organic compound is fixed in a melt of soil and activated alumina or a metal oxide powder with pores in its surface according to the pyrolytic treatment method for halogen-containing organic compounds of this invention, the amount of halogen constituent in the decomposition off-gas is reduced. In addition, since the organic compound from which the halogen constituent was dissociated is chemically reduced and pyrolyzed in the presence of water, the organic compound is efficiently decomposed and the amount of organic compound in the decomposition off-gas is reduced. Consequently, it becomes difficult for dioxins to be produced in the decomposition off-gas.

[Brief Explanation of the Figures]

[Figure 1] This is a sectional diagram showing and example of a heat resistant container filled with contaminated soil.

[Figure 2] This is a sectional diagram of a heat resistant container in which a covering soil layer, an initial conductivity resistance path, and electrodes are disposed.

[Figure 3] This is a plan-view diagram viewed from above the heat resistant container in Figure 2.

[Figure 4] This is a sectional diagram of an example of heat resistant container covered with a hood.

[Figure 5] This is a schematic diagram showing an example of the configuration of a contaminated soil mixture using a melt furnace that employs Joule heat.

[Figure 6] This is a diagram that schematically shows the heat distribution in a contaminated soil mixture when the contaminated soil mixture is heated using a melt furnace that employs Joule heat.

[Legend]

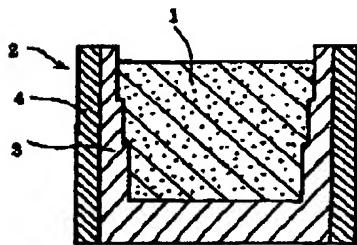
- 1 ... contaminated soil mixture
- 2 ... heat resistant container
- 3 ... inner container
- 4 ... outer container
- 5 ... covering soil layer
- 6 ... initial conductivity resistance path
- 7, 7a, 7b, 7c, 7d ... electrodes
- 8 ... hood
- 9 ... air inlet port
- 10 ... exhaust port
- 11 ... melt furnace
- 12 ... electrical energy supply device
- 13 ... gas treatment device
- 14 ... air heating device
- 15 ... generator
- 16 ... transformer
- 17 ... secondary heating equipment
- 18 ... cooler-dust arrester-cleaner (Venturi scrubber)
- 19 ... HEPA filter
- 20 ... activated charcoal filter

[Abstract]

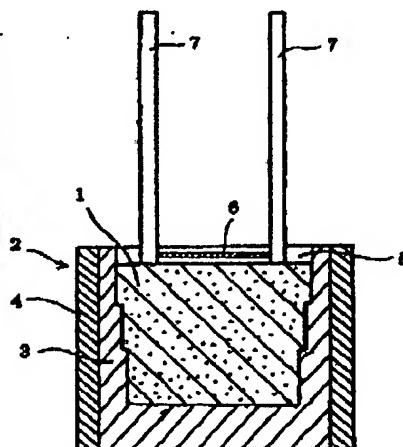
[Problem] To provide a method whereby halogen-containing organic compounds can be pyrolyzed so as to prevent as much as possible the discharge of the halogen constituent (especially chlorine) and benzene to the outside.

[Means of Solution] A pyrolytic treatment for halogen-containing organic compounds in which the halogen-containing organic compound is heated together with soil to a temperature of 300 to 600°C in the presence of a metal oxide powder and water, causing the halogen constituent to dissociate from the halogen-containing organic compound and causing that halogen constituent to be captured in the mixture of soil and metal oxide powder, after which, that mixture is melted, fixing the halogen constituent in the melt and chemically reducing and pyrolyzing the organic compound from which the halogen constituent has been dissociated.

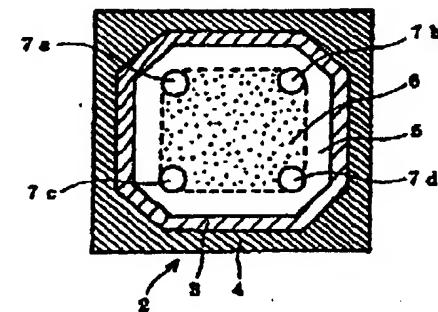
[Fig. 1]



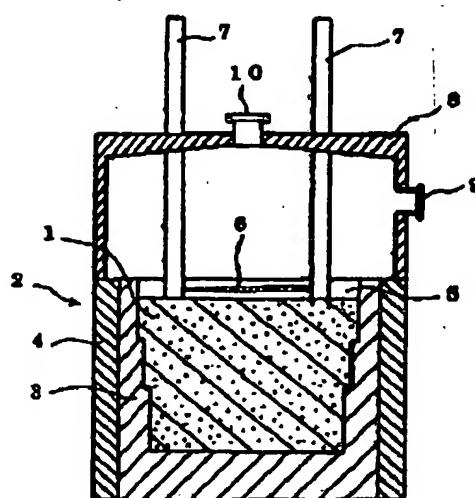
[Fig. 2]



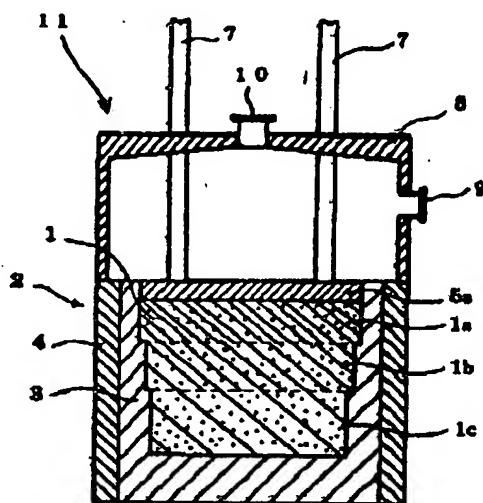
[Fig. 3]



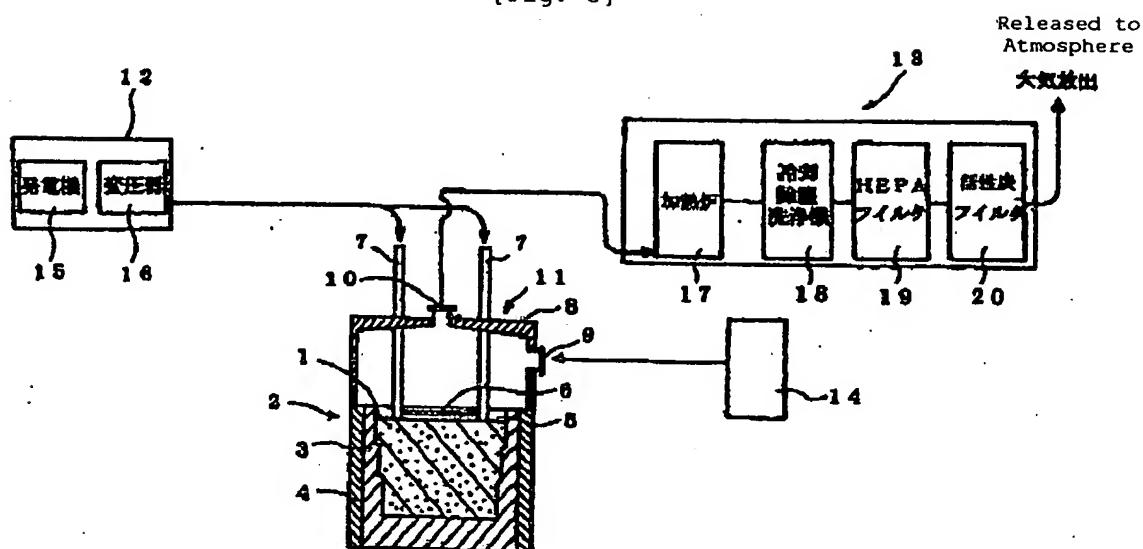
[Fig. 4]



[Fig. 6]



[Fig. 5]



- Key -

- 15 ... Generator
- 16 ... Transformer
- 17 ... Furnace
- 18 ... Cooler-Dust Arrester-Cleaner
- 19 ... HEPA Filter
- 20 ... Activated Charcoal Filter

Continued from front page

(56) Bibliography Japan Kokai Patent Application No. 2001-233621 (JP, A)
 Japan Kokai Patent Application No. 2002-35736 (JP, A)
 Japan Kokai Patent Application No. H04-118414 (JP, A)
 Japan Kokoku Patent Application No. S02-43847 (JP, B1)

(58) Examined Fields (Int. Cl.⁷, DB Name)

B09C 1/06
B09B 3/00
E02D 3/11
A62D 3/00